“SMART” WATER-BASED EPOXY COATINGS FOR CORROSION PROTECTION OF AA2024

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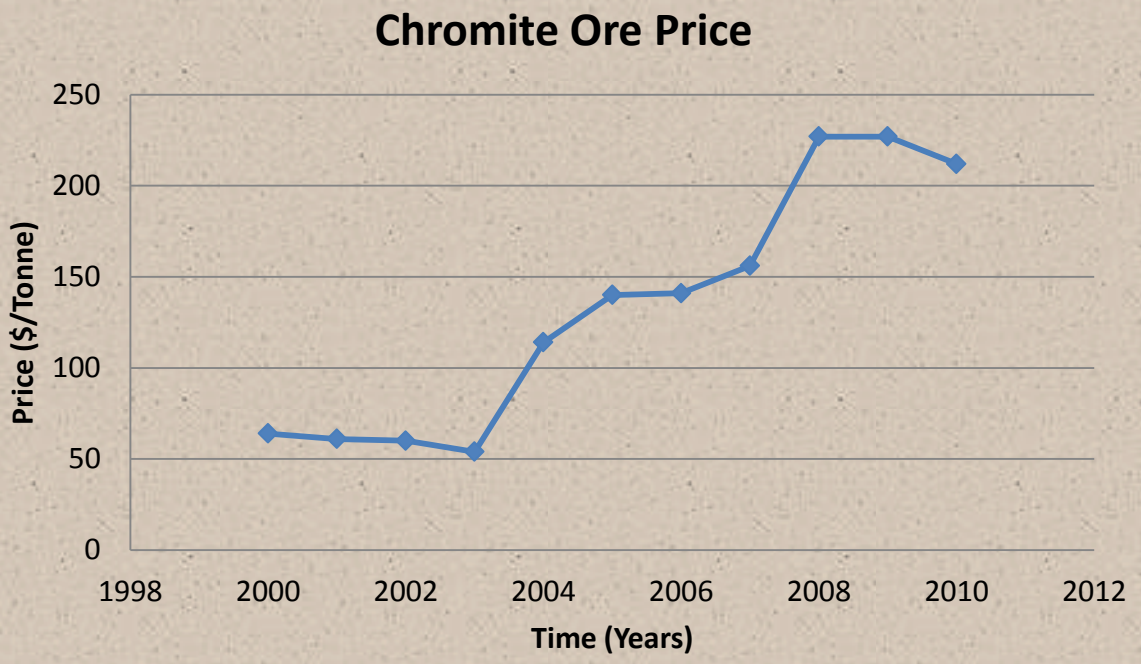
Introduction

Chromium (VI) Surface Treatment:

- Favours the adhesion of organic coatings
- Increases corrosion resistance
- Easy application

- Toxic
- Cancerigenous
- Pollutant
- High elimination cost



(USGS Annual Publications - Mineral Commodity Summaries)

Introduction

Goal

- Develop more effective “smart” coatings for corrosion protection of AA2024

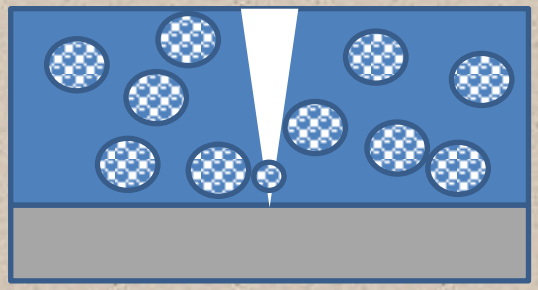
Impact

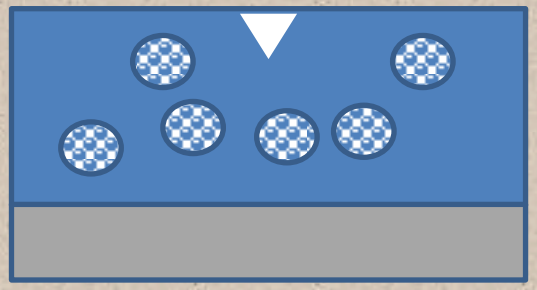
- Elimination of chromate pigments from current formulations used in the aircraft industry;
- Reduced thickness and decreased number of layers;
- Increased corrosion resistance, lifetime and mechanical properties, by addition of “smart” additives, conferring self-healing properties;
- Application to various industries (e.g. aeronautial, automotive, etc.).

Introduction

Healing Processes

Mechanical Trigger





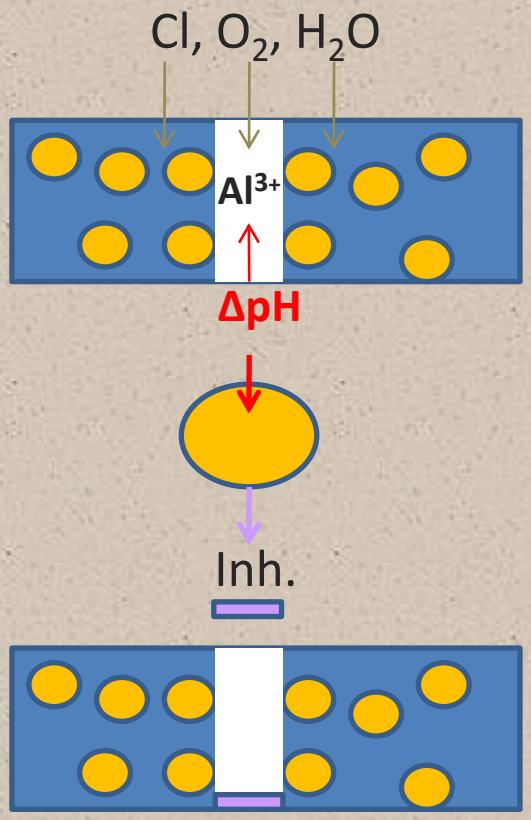
1st - Barrier properties are damaged;

2nd - Corrosion onset;

3rd - Release of healing agents contained in the capsules;

4th - Recovery of the barrier properties

pH Activation

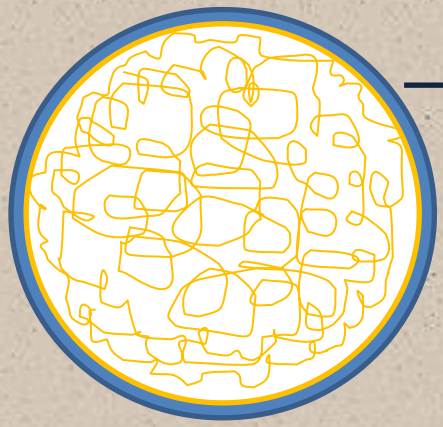


Inhibited area

Introduction

Healing Processes

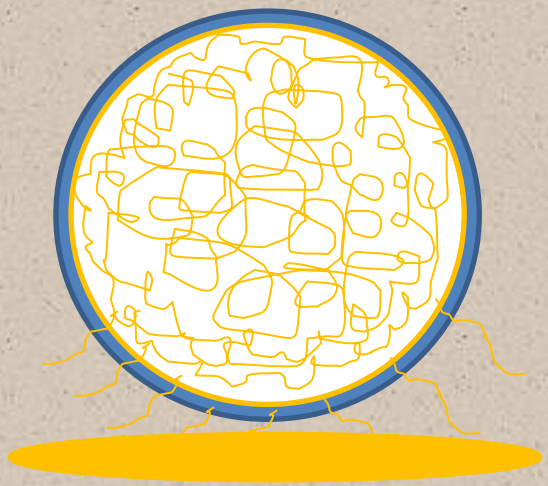
pH Activation



Reservoir filled with corrosion inhibitor

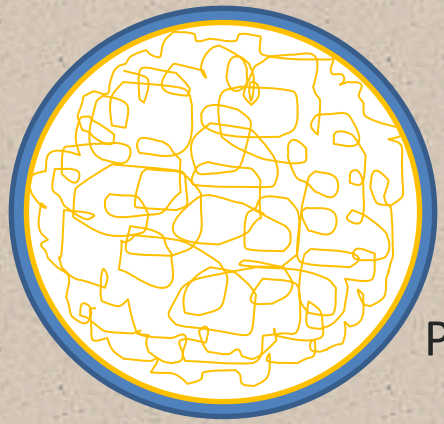
pH sensitive layer senses ⇑ ΔpH on the active surface

Pores open



Inhibiting layer Corrosion stops

sensitive layer detects pH stabilization

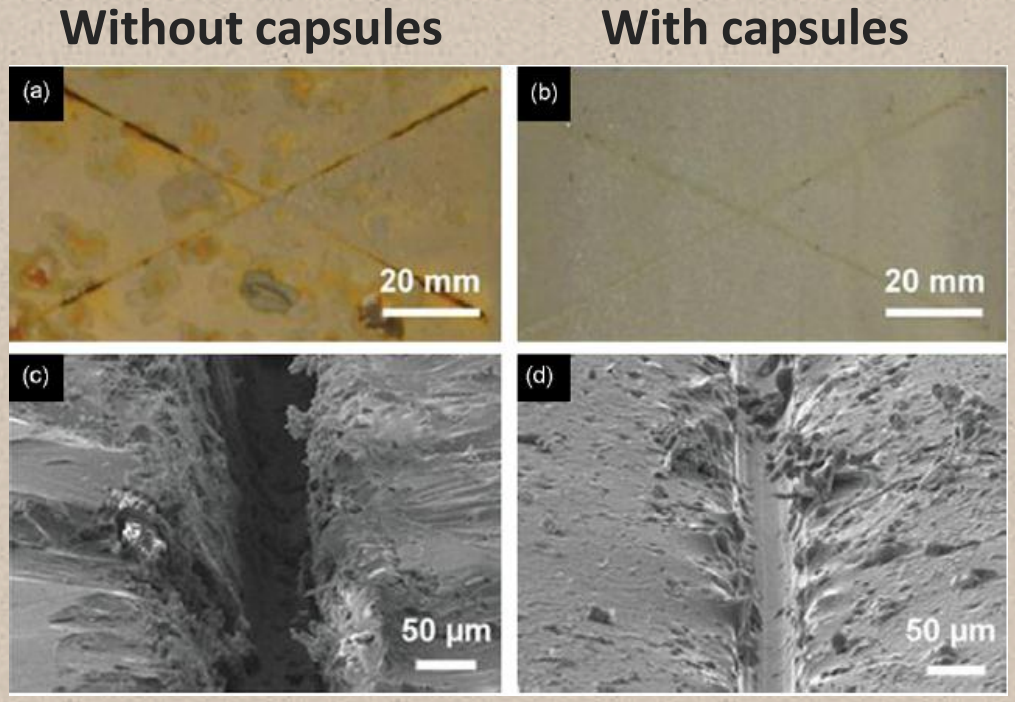


Pores close

Introduction

Healing Processes

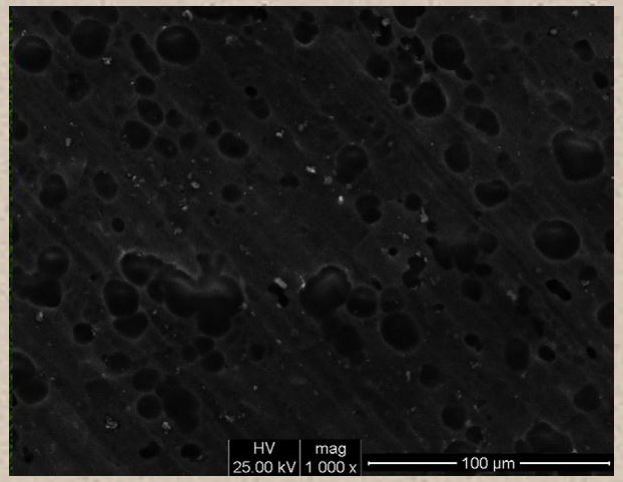
- Stimulus: Mechanical Action
- Response: Capsule rupture – healing by polymerisation



Advanced Materials, **2009**, 21, 645-649

Introduction

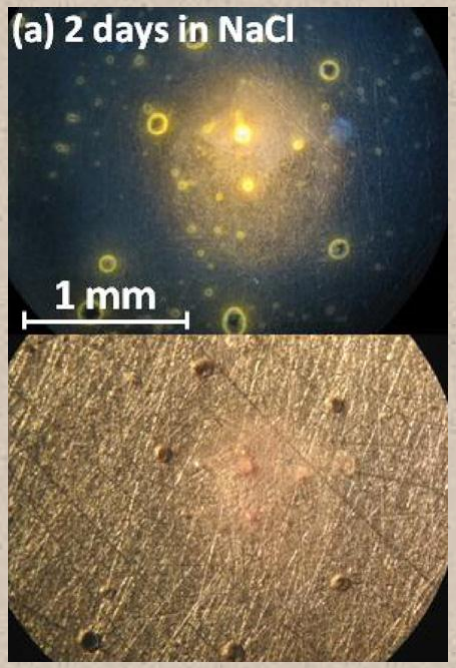
"Smart" Epoxy Coatings



SEM image

TiO_2 nanocontainers loaded with 8-hydroxyquinoline (corrosion inhibitor).

Progress in Organic Coatings, **2012**, 74, 418– 426



Confocal Microscope
(Under UV light)

Early and non-invasive corrosion detection.

Confocal Microscope

Progress in Organic Coatings, **2011**, 71, 406–412

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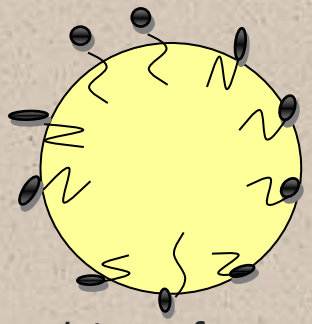
"Smart" Additives

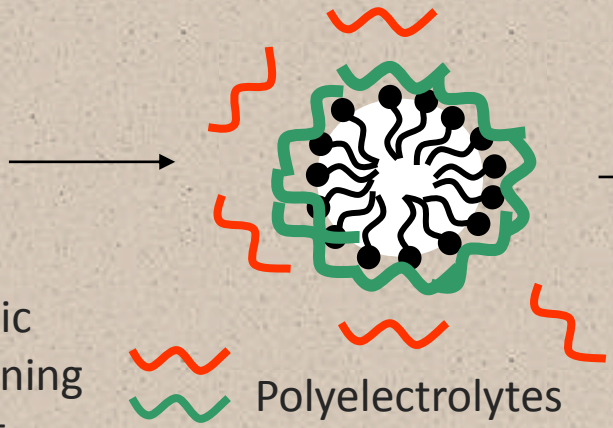
- Compatibility with the host matrix
- Compatible with coating thickness
- Identical/improved barrier properties
- High loading capacity
- Stimuli-responsive
- Long stability

Polyelectrolyte Nanocapsules

Polyelectrolyte (soft) shells - Layer by Layer



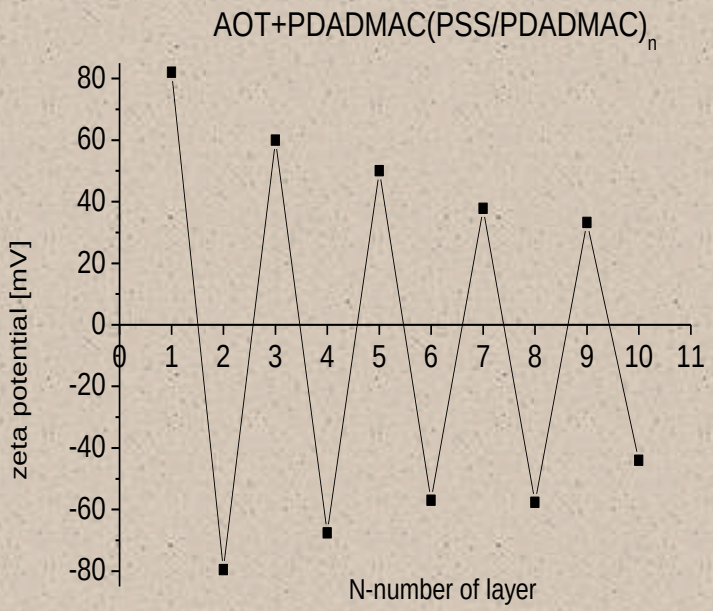
Emulsion of organic solvent/water containing MBT + surfactant



Polyelectrolytes

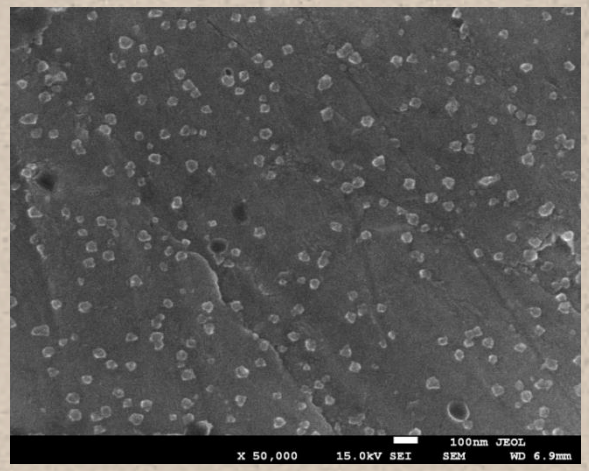
Concentration of MBT 0,03g/L

Layer-by-Layer adsorption of polyelectrolytes



Zeta potential with number of layers

SEM Image



Size ~60nm

Zeta Potential +40mV

Tested Coatings

Tested coatings:

- Coating 1 – Epoxy Resin with 35% of water suspension of negatively charged capsules without inhibitor
- Coating 2 – Epoxy Resin with 35% of water suspension of negatively charged capsules with inhibitor

Used Techniques:

- SEM → Coating Morphology
- EIS
- SVET
- SIET

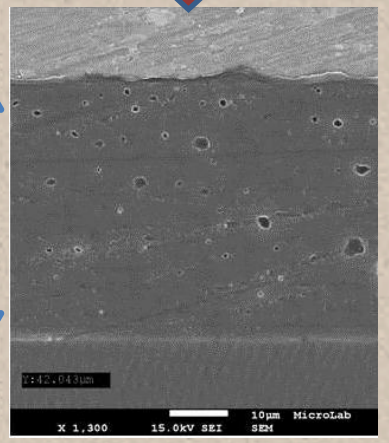
→ Electrochemical Techniques

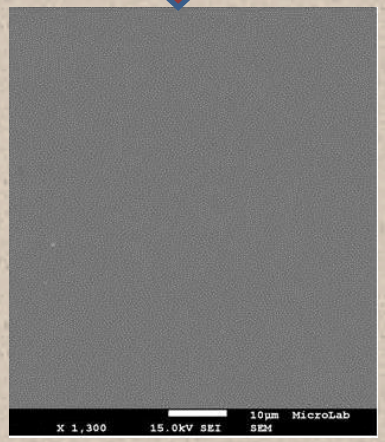
Morphology (SEM images)

Cross-Section

Top View

Thickness = 42µm



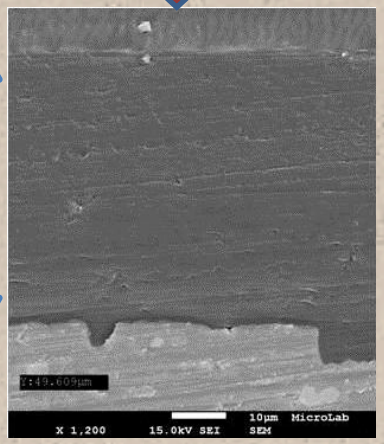


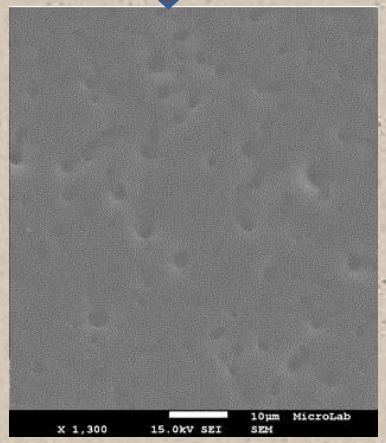
Blank

Cross-Section

Top View

49µm



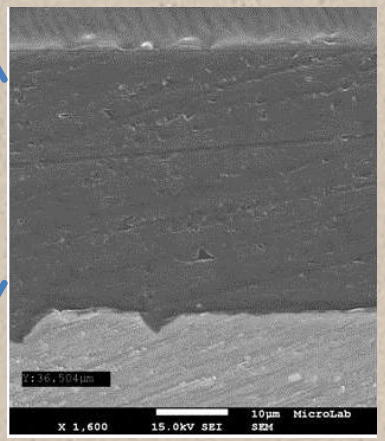


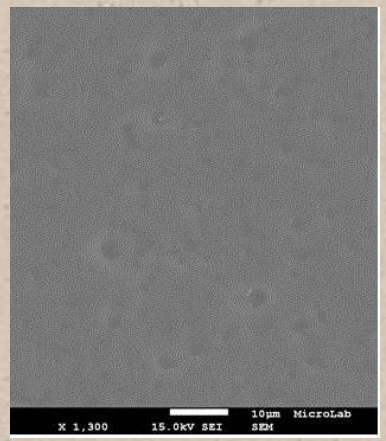
Coating 1

Cross-Section

Top View

37µm

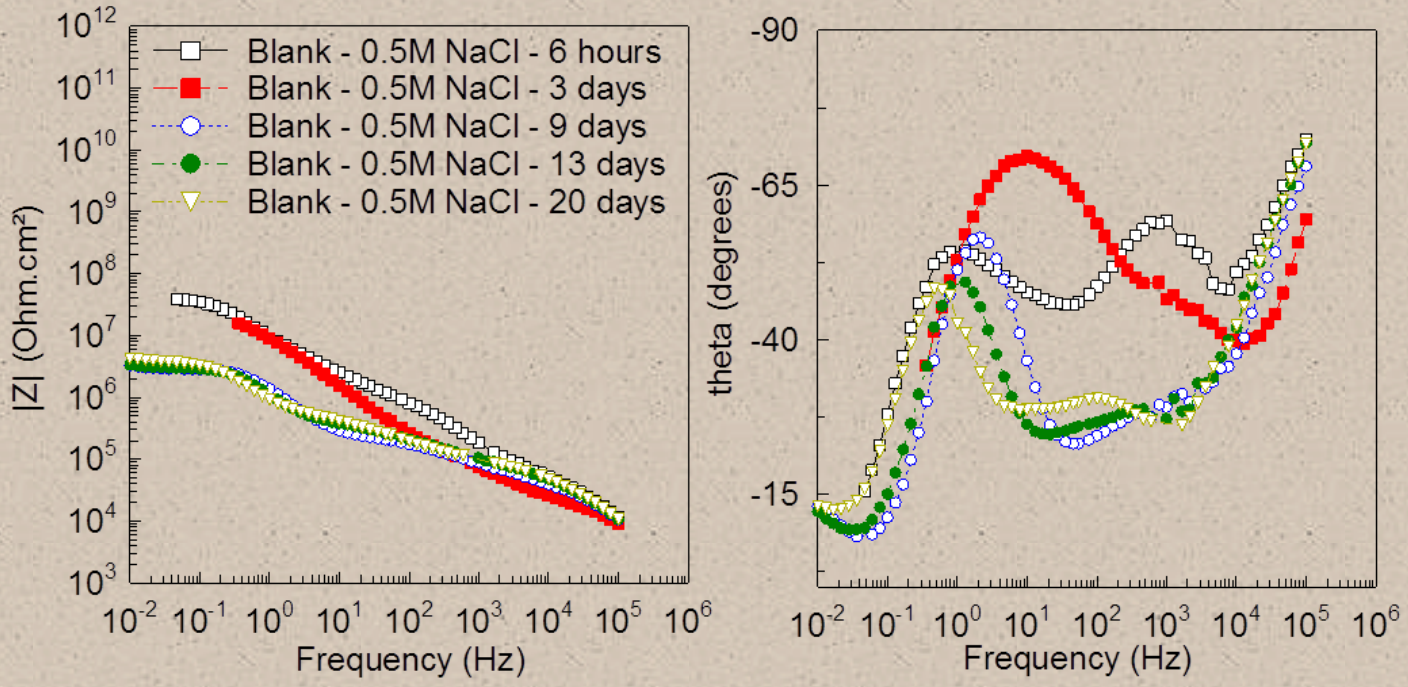




Coating 2

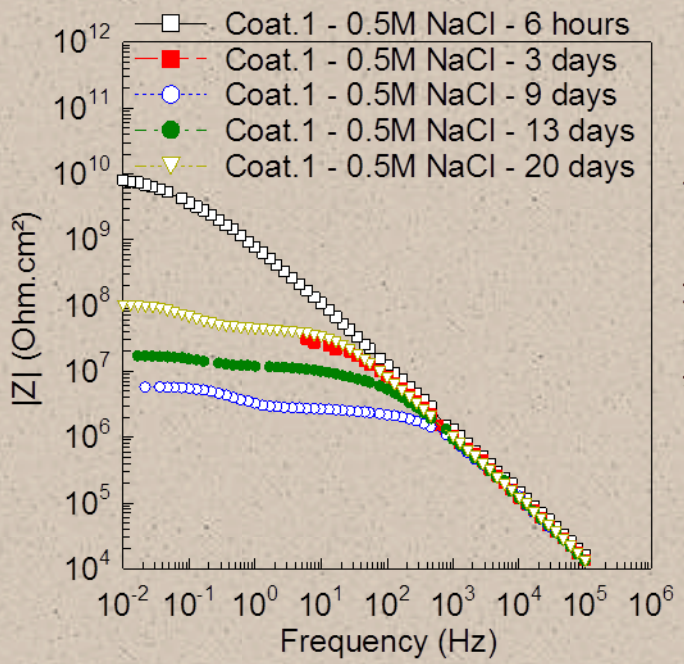
EIS Measurements

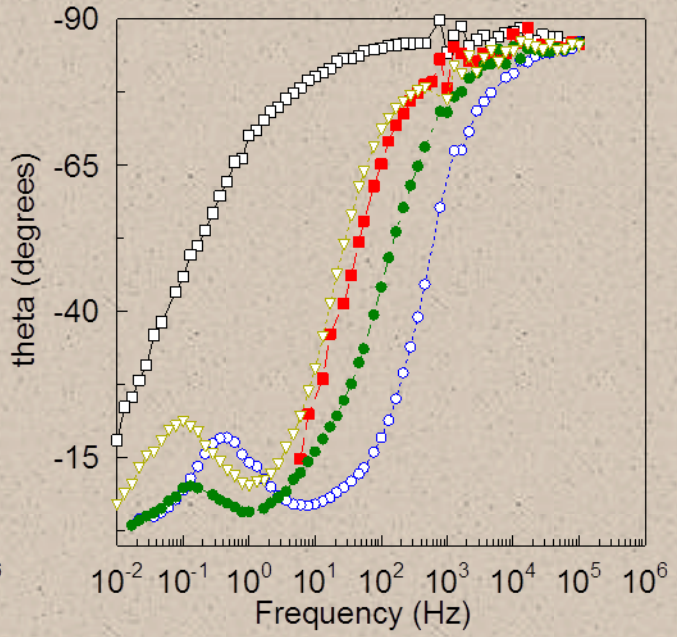
Blank – Epoxy without Nanocapsules



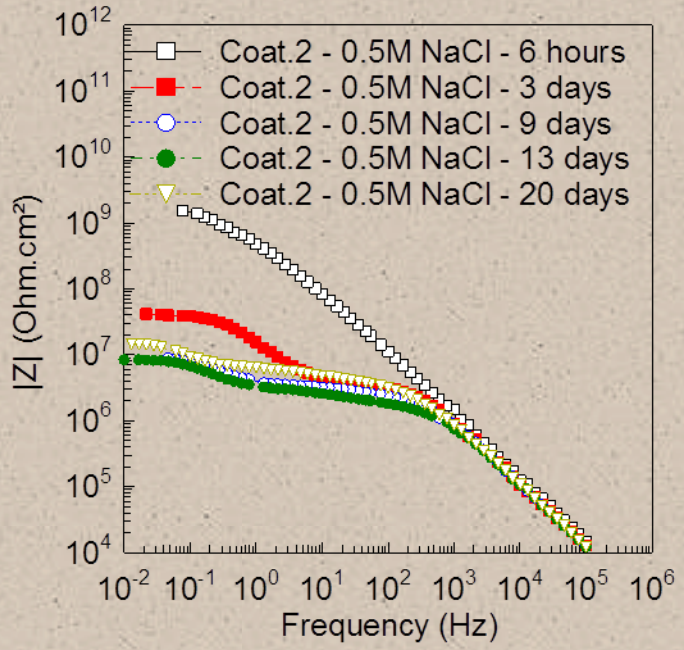
EIS Measurements

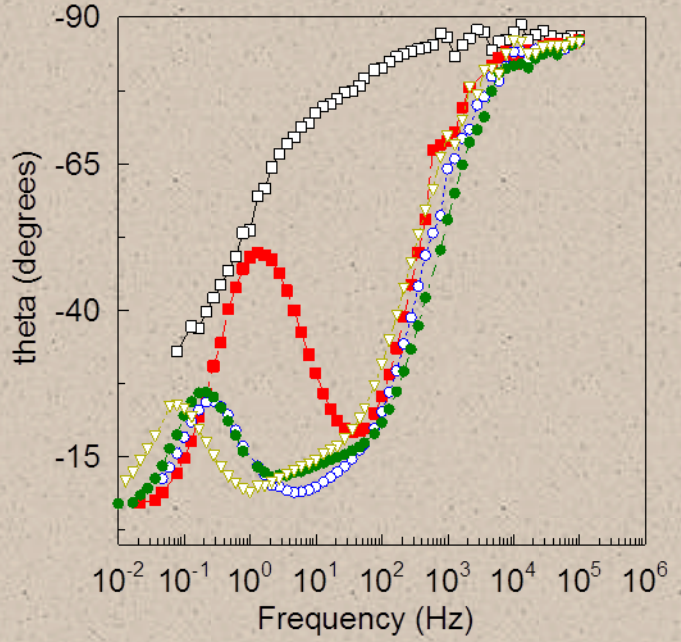
Coating 1 – Epoxy + Empty Nanocapsules



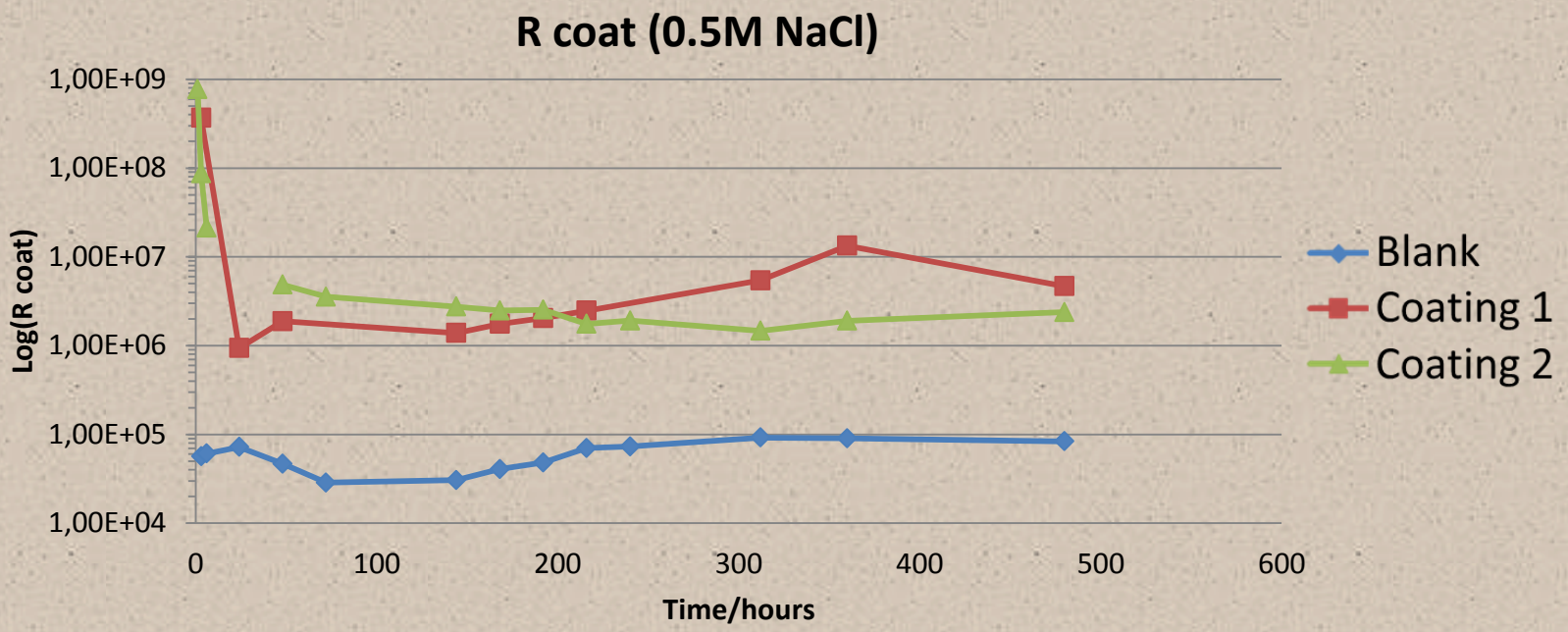


Coating 2 – Epoxy + Nanocapsules with MBT+LI

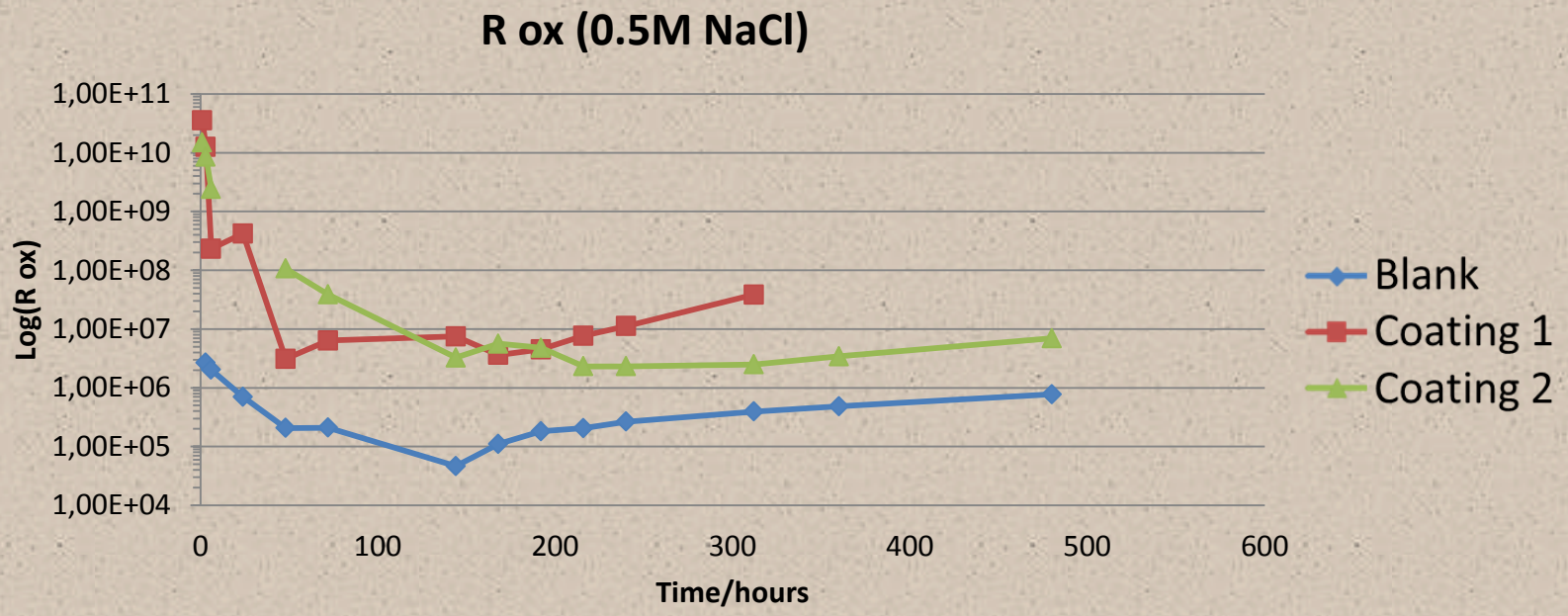




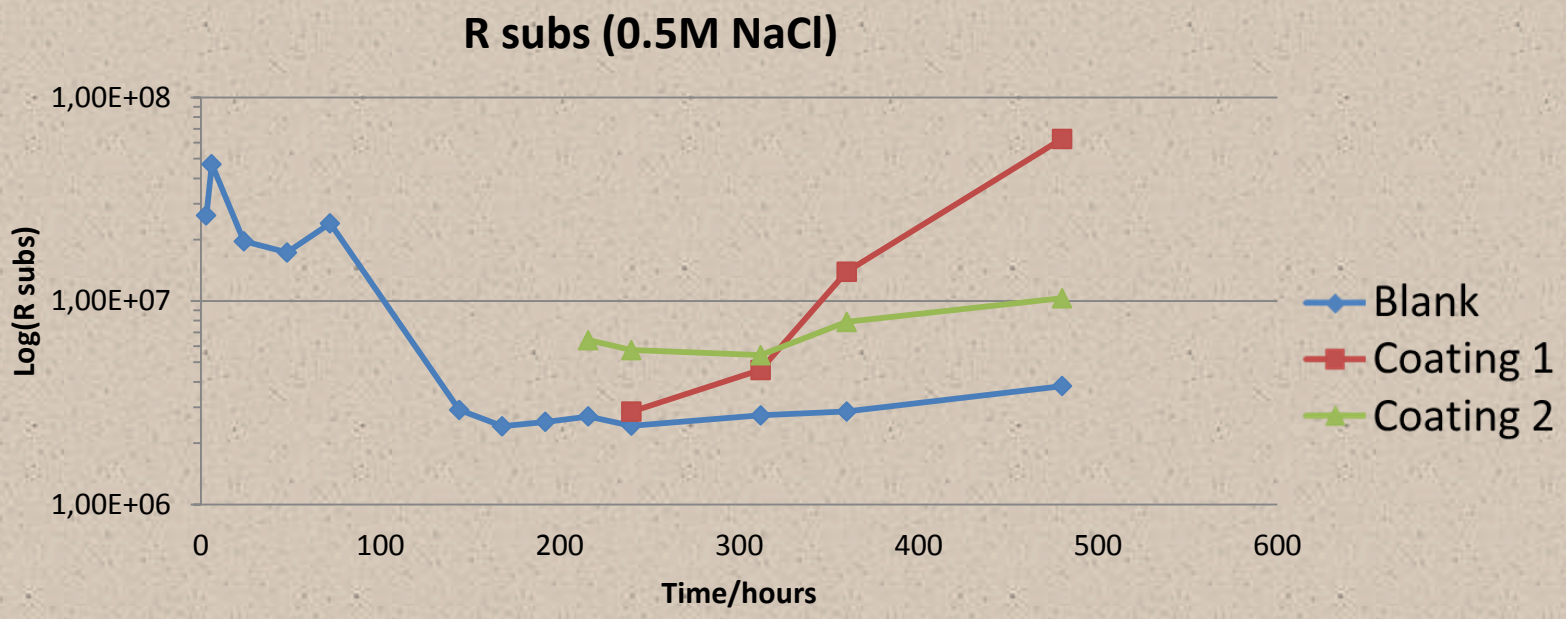
Fittings (Coating Layer)



Fittings (Oxide Layer)



Fittings (Substrate)



Defect (SVET & SIET)

Blank coating

Scan size: W0.9 x H0.96 mm

Difference in pH
1h → 5.9 – 5,5
15h → 6 – 5,3

Δ pH

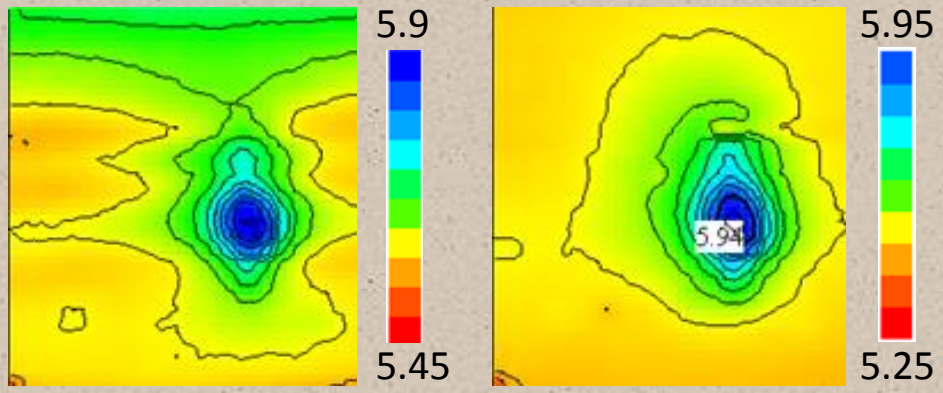
Activity increases

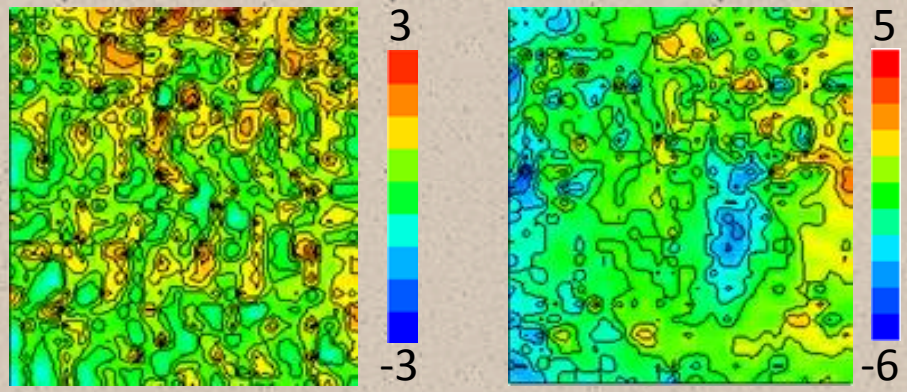
Difference in I
1h → -3 to 3
15h →-6 to 6

Current density

Activity increases

pH map





1h 18h

Current map I = µA/cm²

Defect (SVET & SIET)

Coating + MBT filled nanocapsules

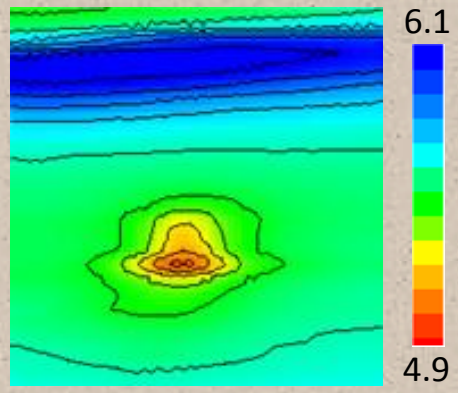
Scan size: W1.0 x H1.1 mm

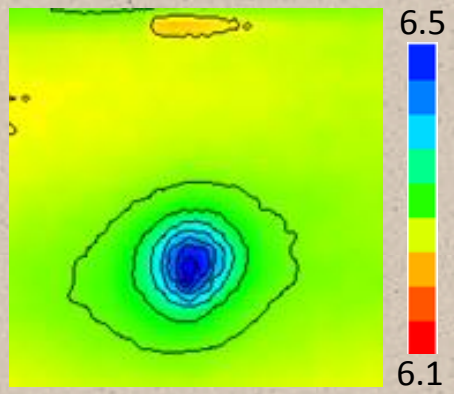
Difference in pH
1h → 6.1 – 4.9
15h →6.5 – 6.2

Δ pH

Activity decreases

pH map

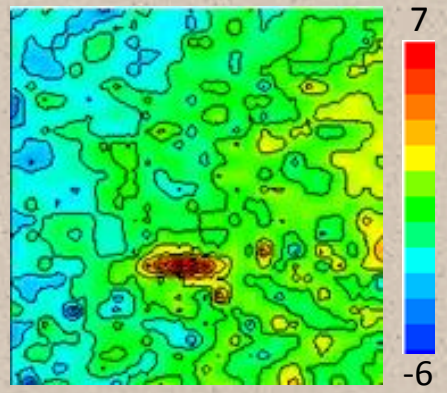


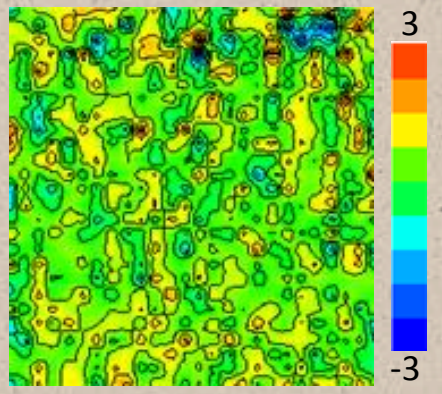


Difference in I
1h → -3 to 3
18h →-6 to 6

Current density

Activity vanishes





2h 18h

Current map I = µA/cm²

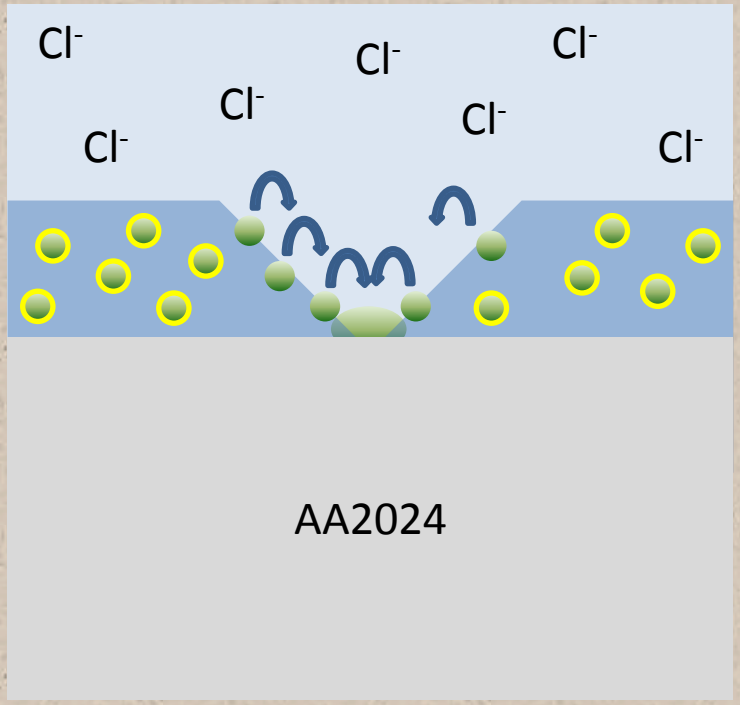
Mechanism of self-healing

Defects open a path for Chloride ions

The corrosion process starts on the damaged oxide

The inhibitors is released because nanocapsules are broken and because their shell is pH sensitive

Inhibition of the corrosion process



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Conclusions

- Allows the use of water as solvent (Green).
- Nanocapsules were successfully prepared and characterised.
- There is a very good compatibility between the nanocapsules and the epoxy based matrix.
- The capsules do not affect greatly the morphology of the coating.
- The coatings embeded with nanocapsules, displayed the best performance.
- A recovery of the low frequency impedance was observed in damaged coatings.
- Localised electrochemical techniques revealed self-healing of the corrosion activity.

Acknowledgements

- MUST project and partners that supplied materials for coatings (EADS and Mankiewicz)

- FLAD

- C3P

Thank You For Your Attention!